Nanoscale, Crystalline Silicon Powder

The present invention relates to a nanoscale, crystalline silicon powder, its production and use.

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Nanoscale silicon powders are of great interest on account of their special optical and electronic properties.

It is known to produce silicon by pyrolysis of silane
10   (SiH_4). In US 4661335 an aggregated, largely polycrystalline silicon powder with a low density and a BET surface of between 1 and 2 m^2/g is described, which is obtained by pyrolysis of silane at temperatures between 500°C and 700°C in a tubular reactor. Such a powder no
15   longer meets present day requirements. The process is furthermore not economical due to the large content of unreacted silane.

In Laser Physics, Vol. 10, pp. 939 – 945 (2000) Kuz´min et
20   al. describe the production of a nanoscale silicon product by means of laser-induced decomposition of silane at reduced pressure. Each individual particle of the powder thereby produced has a polycrystalline core of 3 to 20 nm and an amorphous covering with a diameter of up to 150 nm.
25   No information is given regarding the surface of the silicon powder.

In J. Mater. Sci. Technol., Vol. 11, pp. 71 – 74 (1995) Li et al. describe the synthesis of aggregated,
30   polycrystalline silicon powder by laser-induced decomposition of silane in the presence of argon as diluent gas at atmospheric pressure. No information is given regarding the surface of the silicon powder.

35   In Vacuum, Vol. 45, pp. 1115 – 1117 (1994) Costa et al. describe an amorphous silicon powder whose surface contains a large proportion of hydrogen. The silicon powder is

produced by decomposition of silane by means of a radio-frequency plasma reactor *in vacuo*.

In Jap. J. Appl. Physics, Vol 41, pp. 144 – 146 (2002)
5   Makimura et al. describe the production of hydrogen-containing silicon nanoparticles by laser attrition of a silicon target *in vacuo* in the presence of hydrogen and neon.   No information is given as to whether the silicon nanoparticles exist in crystalline or amorphous form.
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EP-A-680384 describes a process for the deposition of a non-polycrystalline silicon on a substrate by decomposition of a silane in a microwave plasma at reduced pressure.   No information is given regarding the surface properties of
15   the silicon.

It is known to produce aggregated, nanoscale silicon powder in a hot-wall reactor (Roth et al., Chem. Eng. Technol. 24 (2001), 3).   A disadvantage of this process is that the
20   desired crystalline silicon occurs together with amorphous silicon, which is formed by reaction of the silane on the hot reactor walls.   The crystalline silicon in addition has a low BET surface of less than 20 m²/g and is thus as a rule too coarse for electronic applications.   Furthermore
25   no process is described by Roth et al. in which doped silicon powders are obtained.   Such doped silicon powders are, on account of their semiconductor properties, of great importance in the electronics industry.   A disadvantage however is that silicon powder is deposited on the reactor
30   walls and acts as an insulator.   The temperature profile in the reactor consequently changes, and thus also the properties of the silicon powder that is produced.

The prior art demonstrates the intense interest in silicon
35   powders.   The object of the present invention is to provide a silicon powder that avoids the disadvantages of the prior art.   In particular, the silicon powder should be one

having a uniform modification. The powder should be
capable of meeting the growing demands for miniaturisation
in the production of electronic components.

5   The object of the invention is also a process for the
production of this powder.

The present invention provides an aggregated, crystalline
silicon powder that is characterised in that it has a BET

10   surface of more than 50 m²/g.

In a preferred embodiment the silicon powder according to
the invention may have a BET surface of 100 to 700 m²/g,
the range from 200 to 500 m²/g being particularly

15   preferred.

The term aggregated is understood to mean that spherical or
largely spherical primary particles, such as for example as
are first of all formed in the reaction, coalesce to form

20   aggregates during the further course of the reaction. The
degree of coalescence of the aggregates can be influenced
by the process parameters. These aggregates may form
agglomerates during the further course of the reaction. In
contrast to the aggregates, which as a rule cannot be

25   decomposed, or only partially so, into the primary
particles, the agglomerates form an only loose concretion
of aggregates.

The term crystalline is understood to mean that at least

30   90% of the powder is crystalline. Such a degree of
crystallinity can be determined by comparing the
intensitites of the [111],[220] and [311] signals of the
powder according to the invention with a silicon powder of
known crystallinity and crystal size.

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Within the context of the invention a silicon powder with a
crystalline fraction of at least 95%, particularly

preferably with a crystalline fraction of at least 98%, is
preferred. The evaluation of TEM images and counting of
the primary particles that exhibit lattice grid lines as a
feature of the crystalline state are suitable for
5   determining the degree of crystallinity.

The silicon powder according to the invention may have a
hydrogen loading of up to 10 mole %, a range from 1
to 5 mole % being preferred. NMR spectroscopy methods, such
10   as for example ^{1}H-MAS-NMR spectroscopy, or IR spectroscopy
are suitable for determining the degree of saturation.

Furthermore the silicon powder according to the invention
may be doped. The following elements may preferably be
15   employed as doping components, especially for use as
semiconductors in electronics components: phosphorus,
arsenic, antimony, bismuth, boron, aluminium, gallium,
indium, thallium, europium, erbium, cerium, praseodymium,
neodymium, samarium, gadolinium, terbium, dysprosium,
20   holmium, thulium, ytterbium or lutetium. The proportion of
these elements in the silicon powder according to the
invention may be up to 1 wt.%. As a rule a silicon powder
may be desirable in which the doping component is contained
in the ppm or even ppb range. A range from 10^{13} to 10^{15}
25   atoms of doping component/cm^3 is preferred.

In addition it is possible for the silicon powder according
to the invention to contain lithium as doping component.
The proportion of lithium in the silicon powder may be up
30   to 53 wt.%. Silicon powders with up to 20 to 40 wt.% of
lithium may be particularly preferred.

Likewise, the silicon powder according to the invention may
contain germanium as doping component. In this case the
35   proportion of germanium is up to 40 wt.%. Silicon powders
containing 10 to 30 wt.% of germanium may be particularly
preferred.

Finally, the elements iron, ruthenium, osmium, cobalt, rhodium, iridium, nickel, palladium, platinum, copper, silver, gold and zinc may also be used as doping component
5 of the silicon powder. Their proportion may be up to 5 wt.% of the silicon powder.

The doping component may in this connection be distributed homogeneously in the powder, or may be concentrated or
10 intercalated in the covering or in the core of the primary particles. The doping components may preferably be incorporated at lattice sites of the silicon. This depends substantially on the nature of the doping substance and the reaction conditions.
15

The term doping component is understood within the context of the invention to denote the element present in the powder according to the invention. The term doping substance is understood to denote the compound that is used
20 in the process in order to obtain the doping component.

The present invention also provides a process for the production of the silicon powder according to the invention, which is characterised in that
25
- at least one vaporous or gaseous silane and optionally at least one vaporous or gaseous doping substance,

- together with an inert gas
30
- are continuously transferred to a reactor and mixed therein,

- wherein the proportion of the silane is between
35 0.1 and 90 wt.% referred to the sum total of silane, doping substance and inert gases,

- and a plasma is produced by input of energy by means of electromagnetic radiation in the microwave range at a pressure of 10 to 1100 mbar,

5   - the reaction mixture is allowed to cool or is cooled and the reaction product is separated in the form of a powder from gaseous substances.

The process according to the invention is characterised in
10   that a stable plasma is produced that leads to a very uniform product and, in contrast to processes that operate in a high vacuum, allows high conversion rates. As a rule the conversion of silane is at least 98%.

15   The process according to the invention is carried out so that the proportion of silane, optionally with the inclusion of the doping component, in the gas stream is between 0.1 and 90 wt.%. A high silane content leads to a high throughput and is therefore economically sensible.
20   With very high silane contents however a formation of larger aggregates is to be expected. A silane content of between 1 and 10 wt.% is preferred in the context of the invention. At this concentration aggregates with a diameter of less than 1 μm are as a rule obtained.
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Within the context of the invention a silane may be a silicon-containing compound that yields silicon, hydrogen, nitrogen and/or halogens under the reaction conditions. SiH_4, Si_2H_6, $ClSiH_3$, Cl_2SiH_2, Cl_3SiH and/or $SiCl_4$ may
30   preferably be used, SiH_4 being particularly preferred. In addition it is also possible to use $N(SiH_3)_3$, $HN(SiH_3)_2$, $H_2N(SiH_3)$, $(H_3Si)_2NN(SiH_3)_2$, $(H_3Si)NHNH(SiH_3)$ or $H_2NN(SiH_3)_2$.

A doping substance within the meaning of the invention may
35   be a compound that contains the doping component covalently or ionically bonded and that yields the doping component, hydrogen, nitrogen, carbon monoxide, carbon dioxide and/or

halogens under the reaction conditions. There may
preferably be used hydrogen-containing compounds of
phosphorus, arsenic, antimony, bismuth, boron, aluminium,
gallium, indium, thallium, europium, erbium, cerium,
5   praseodymium, neodymium, samarium, gadolinium, terbium,
dysprosium, holmium, thulium, ytterbium, lutetium, lithium,
germanium, iron, ruthenium, osmium, cobalt, rhodium,
iridium, nickel, palladium, platinum, copper, silver, gold
or zinc. Particularly preferred are diborane and phosphane
10   or substituted phosphanes such as $tBuPH_2$, tBu_3P, $tBuPh_2P$ or
$tBuPh_2P$ and trismethylaminophosphane $((CH_3)_2N)_3P$. In the
case where lithium is used as doping component, it has
proved most convenient to employ the metal lithium or
lithium amide $(LiNH_2)$ as doping substance.
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As inert gas there may mainly be used nitrogen, helium,
neon or argon, argon being particularly preferred.

The energy input is not limited. Preferably the energy
20   input should be chosen so that the back-scattered,
unabsorbed microwave radiation is minimal and a stable
plasma is formed. As a rule, in the process according to
the invention the power input is between 100 W and 100 KW,
and particularly preferably between 500 W and 6 KW. In
25   this connection the particle size distribution may be
varied by the radiated microwave energy. Thus, for
identical gas compositions and volume flows, higher
microwave energies may lead to a smaller particle size and
to a narrower particle size distribution.
30
Fig. 1A shows the particle size distribution determined
using a differential mobility analyser (DMA), at 220 and
360 W emitted microwave output, a total volume flow of
4000 sccm and an SiH_4 concentration of 0.375 %. In
35   addition to a smaller mean particle size and a sharper

particle size distribution, the start of the particle
distribution is also shifted to smaller values.

5   Fig. 1B shows a detail of incipient particle growth for a
synthesis at 8000 sccm total volume flow, a radiated
microwave energy of 540 and 900 W and an SiH_4 concentration
of 0.375 %.

Figs. 1A and 1B show qualitatively the same result. By
10   comparing the two it is clear that at higher volume flows
more energy must be made available in order to produce
particles of comparable size. The plotted numerical values
are not comparable with one another since different
dilution stages had to be employed to adapt the measurement
15   process.

The pressure range in the process according to the
invention is between 10 mbar and 1100 mbar. This means
that a higher pressure as a rule leads to a silicon powder
20   according to the invention with a lower BET surface, while
a lower pressure leads to a silicon powder according to the
invention with a larger surface. Thus, in a range of up to
100 mbar, large surface area silicon powders with a BET
surface of up to 700 m^2/g can be obtained, whereas in a
25   range from ca. 900 up to 1100 mbar, silicon powders with a
BET surface of 50 up to 150 g/m^2 can be obtained.

Microwave range is understood in the context of the
invention to denote a range from 900 MHz to 2.5 GHz, a
30   frequency of 915 MHz being particularly preferred.

The cooling of the reaction mixture may for example take
place by an external wall cooling of the reactor or by
introducing inert gas.

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Preferably the process according to the invention may be
carried out in such a way that hydrogen, optionally in a
mixture with an inert gas, is additionally introduced into
the reactor. The proportion of hydrogen may lie in a range

5   from 1 to 96 vol.%

It may furthermore be advantageous to carry out the process
according to the invention so that the reaction mixture
that is produced by the input of energy by means of

10   electromagnetic radiation in the microwave range at a
pressure of 10 to 1100 mbar is thermally post-treated.
Reaction mixture is in this context understood to denote
the mixture consisting of the silicon powder according to
the invention and further reaction products as well as

15   unreacted starting products.

The aggregate structure, the BET surface and possibly the
hydrogen content of the silicon powder may be varied by the
thermal post-treatment. Likewise the thermal post-

20   treatment may lead to an increase in the crystallinity of
the silicon powder or the density of defects in the crystal
lattice may be reduced.

The thermal post-treatment may be carried out in the

25   presence of at least one doping substance, the doping
substance being introduced together with an inert gas
and/or hydrogen.

Particularly preferably a wall-heated hot-wall reactor may

30   be used for the thermal post-treatment of the reaction
mixture, the hot-wall reactor being dimensioned so that a
chosen doping substance is decomposed and may be
incorporated as doping component in the silicon powder.
Depending on this, the residence time in the hot-wall

35   reactor is between 0.1 sec and 2 sec, preferably between
0.2 sec and 1 sec. This type of doping is preferably used
with only low degrees of doping. The maximum temperature

in the hot-wall reactor is preferably chosen so that it
does not exceed 1000°C.

In addition to the thermal post-treatment of the reaction
5   mixture it is also possible to obtain a silicon powder
according to the invention by thermal post-treatment of the
reaction product that is present after the energy input by
means of electromagnetic radiation in the microwave range
at a pressure of 10 to 1100 mbar followed by cooling and
10   separation of gaseous substances. In this connection it is
also possible to carry out the thermal post-treatment in
the presence of at least one doping substance.

Figs. 2A-C illustrate the possible embodiments of the
15   process according to the invention, in which a = silane,
b = inert gas, c = doping substance, d = hydrogen.
Furthermore A = microwave reactor, B = thermal post-
treatment, C = separation of the silicon powder from
gaseous reaction products. The doping substance c is as a
20   rule introduced with an inert gas. Fig. 2A shows an
arrangement in which only a microwave reactor is employed,
while Figs. 2B and 2C include a thermal post-treatment.

A section of Fig. 2A shows the production of the silicon
25   powder from the two essential constituents for the process
according to the invention, namely silane and inert gas.
In addition Fig. 2B illustrates the thermal post-treatment
of the reaction mixture from the microwave reactor with
subsequent separation of the silicon powder.
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Fig. 2C illustrates the thermal post-treatment of the
silicon powder that was separated in a preceding step from
gaseous reaction products and starting substances. The
process according to the invention may preferably be
35   carried out as illustrated in Fig. 2A.

The present invention also provides for the use of the
powder according to the invention for producing electronic
components, electronic circuits and electrically active
fillers.

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Examples:

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Analysis: The BET surface is determined according to DIN
66131. The degree of doping is determined by means of glow
discharge mass spectrometry (GDMS). The hydrogen loading
is determined by means of ^{1}H-MAS-NMR spectroscopy.

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Apparatus: A microwave generator (Muegge company) is used to
produce the plasma. The microwave radiation is focussed in
the reaction space by means of a tuner (3-rod tuner). A
stable plasma is generated in the pressure range from

20 10 mbar up to 1100 mbar and at a microwave output of 100
to 6000 W by the design of the wave guide, the fine
adjustment by means of the tuner and the accurate
positioning of the nozzle acting as electrode.

25 The microwave reactor consists of a quartz glass tube of
30 mm diameter (external) and a length of 120 mm, which is
employed in the plasma applicator.

A hot-wall reactor may be connected downstream of the
30 microwave reactor. For this, a longer quartz glass tube
with a length of 600 mm is used. The mixture leaving the
microwave reactor is heated by an externally heated
zone (length ca. 300 mm).

35 <u>Example 1:</u>
An SiH_4/argon mixture (mixture 1) of 100 sccm (standard
centimetre cube per minute; 1 sccm = 1 cm^3 gas per minute

referred to 0°C and atmospheric pressure) of SiH_4 and
900 sccm of argon as well as a mixture of 10000 sccm of
each of argon and hydrogen (mixture 2), are fed through a
two-fluid nozzle to the microwave reactor. An output of
5 500 W from a microwave generator is fed to the gaseous
mixture and a plasma is thereby produced. The plasma flare
leaving the reactor through a nozzle expands into a space
whose volume of ca. 20 l is large compared to the reactor.
The pressure in this space and in the reactor is adjusted
10 to 200 mbar. The pulverulent product is separated from
gaseous substances in a downstream-connected filter unit.

The powder obtained has a BET surface of $130m^2/g$. Fig. 3
shows the X-ray diffraction diagram of the silicon powder.

15 Examples 2 to 7 are carried out analogously to Example 1,
though with altered parameters. These are given in
Table 1.

Example 5 describes the production of a boron-doped silicon
20 powder. For this, a diborane/argon mixture (0.615% B_2H_6 in
argon) is additionally mixed in with the mixture 1. The
degree of doping determined by means of GDMS corresponds to
the added amount of diborane.

25 Example 6 describes the production of a phosphorus-doped
silicon powder. For this, a tri-tert.-butylphosphane/
argon mixture (0.02 % $(tBu)_3P$) in argon) is in addition
mixed in with the mixture 1. The degree of doping
determined by means of GDMS corresponds to the added amount
30 of tri-tert.-butylphosphane.

Example 7 shows the production of a silicon powder by means
of a combination of microwave reactor and hot-wall reactor.
In contrast to Example 4, which was carried out using only
35 a microwave reactor, the BET surface of the silicon powder
is reduced slightly. In addition the intensity of the IR

signals at 2400 cm^{-1} and 2250 cm^{-1} are significantly reduced
compared to Example 4, whereas the intensity of the signal
at 2100 cm^{-1} is increased.

5   The advantages of the silicon powder according to the
     invention are the following: it is nanoscale, crystalline
     and has a large surface, and can be doped. According to
     XRD and TEM images it is free of amorphous constituents and
     the BET surface may assume values of up to 700 m^2/g.

Table 1: Process parameters and physicochemical values of the silicon powders

Example		1	2	3	4	5	6	7
Mixture 1								
SiH_4	sccm	100	8	50	10	100	100	10
Argon	sccm	900	72	1950	90	1890	1600	90
B_2H_6	sccm	-	-	-	-	10	-	-
$(tBu)_3P$	sccm	-	-	-	-	-	300	-
Mixture 2								
Hydrogen	sccm	10000	100	2000	7500	10000	10000	7500
Argon	sccm	10000	8000	8000	200	10000	10000	200
Microwave output	W	500	300	1500	540	1000	1000	540
Pressure	mbar	200	30	20	1040	200	200	1040
Temperature of hot-wall reactor	°C	-	-	-	-	-	-	900
BET Si powder	m^2/g	130	567	650	63	132	129	56
H loading	mole %	1.5	n.d.	2.7	n.d.	n.d.	n.d.	n.d.
Degree of doping	ppm	-	-	-	-	1200	620	-

n.d. = not determined